

PATENT ABSTRACTS OF JAPAN(11)Publication number : **06-260184**(43)Date of publication of application : **16.09.1994**

| | |
|-------------|-----------|
| (51)Int.Cl. | H01M 8/02 |
| | H01M 8/10 |

(21)Application number : **05-067646**(71)Applicant : **ASAHI GLASS CO LTD**(22)Date of filing : **03.03.1993**(72)Inventor : **TAMURA MASAYUKI
JITSUKATA KIYOSHIGE
MIYAKE HARUHISA**

(54) FUEL CELL WITH SOLID HIGHPOLYMER ELECTROLYTE**(57)Abstract:**

PURPOSE: To provide a high performance fuel cell which uses a solid high- polymer electrolyte having a low electric resistance.

CONSTITUTION: The solid electrolyte used consists of a positive ion exchange film which is made from a perfluorocarbon polymeride film having an AC specific resistance value of $5 \cdot 10^{-11} \Omega \cdot \text{cm}$.

LEGAL STATUS

[Date of request for examination] 02.03.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's withdrawal decision of rejection or application converted registration]

[Date of final disposal for application] 22.07.2002

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2000 Japan Patent Office

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The solid-state polyelectrolyte type fuel cell characterized by having the current-ratio resistance whose above-mentioned cation exchange membrane is 5-11-ohmcm in the fuel cell which uses as a solid-state polyelectrolyte type the cation exchange membrane which consists of a perfluoro carbon polymer which has a sulfonic group.

[Claim 2] The solid-state polyelectrolyte type fuel cell of the claim 1 whose thickness of a cation exchange membrane is 30-300 micrometers.

[Claim 3] A perfluoro carbon polymer is $\text{CF}_2=\text{CF}_2$. The claim 1 or 2 solid-state polyelectrolyte type fuel cells which consist of a copolymer with $\text{CF}_2=\text{CF}-(\text{OCF}_2\text{CFX})_m-\text{Oq}-(\text{CF}_2)_n-\text{A}$ (inside of a formula $m=0-3$, $n=0-12$, $q=0$ or 1 , $X=\text{F}$ or CF_3 , $\text{A}=\text{sulfonic-acid type functional group}$).

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to a solid-state polyelectrolyte type fuel cell.

[0002]

[Description of the Prior Art] Research of the fuel cell (solid-state polyelectrolyte type fuel cell) using the poly membrane of proton conductivity as an electrolyte is progressing in recent years. A solid-state polyelectrolyte type fuel cell operates at low temperature, has the feature that power density can be high and can be miniaturized, and is seen as a hopeful to uses, such as a power supply for mount.

[0003]

[Problem(s) to be Solved by the Invention] The poly membrane used for the above-mentioned use excels [cation exchange membrane / which consists of a perfluoro carbon polymer which proton conductivity ion exchange membrane with a thickness of 100-200 micrometers is usually used, and has especially a sulfonic group] in a basic property, and it inquires widely. However, the electric resistance of the cation exchange membrane proposed now cannot say that it is low not necessarily enough from a viewpoint which obtains the cell of high power density more.

[0004] Although the method of reducing the electric resistance of a cation exchange membrane has the increase in sulfonic group concentration, and reduction of thickness, the remarkable increase in sulfonic group concentration reduces a membranous mechanical strength, or in long-term operation, a film becomes easy to carry out the creep of it, and the problem of reducing endurance produces it. On the other hand, reduction of thickness reduces a membranous mechanical strength, or the problem of reducing processability and handling nature, such as junction to a gas diffusion electrode, further produces it. In this way, development of a cation exchange membrane with a high mechanical strength with low and electric resistance was desired.

[0005]

[Means for Solving the Problem] this invention is made that the above-mentioned **** should be solved, and the solid-state polyelectrolyte type fuel cell characterized by having the current-ratio resistance whose cation exchange membrane is 5-11-ohmcm is offered in the fuel cell which makes the cation exchange membrane of the perfluoro carbon polymer containing a sulfonic group a solid-state polyelectrolyte.

[0006] By this invention, the current-ratio resistance of a cation exchange membrane is measured about the cation exchange membrane (an ion exchange group is an acid type) immersed at 25 degrees C into the sulfuric-acid solution of 1M for 24 hours, and is computed like several 1.

[0007]

[Equation 1] Current-ratio resistance (ω_{cm}) = resistance (ω) x film effective-area (cm^2) / thickness (cm)

[0008] Since a membrane resistance goes up by this invention when the current-ratio resistance of a cation exchange membrane is larger than the above-mentioned upper limit, the output of a cell declines, and film intensity and film handling nature fall on the other hand in being smaller than a lower limit, it is not desirable. Especially current-ratio resistance has desirable 6-10-ohmcm especially.

[0009] Carrying out a membranous degree of swelling to 50 - 90% of the weight in the hydrolysis processing which introduces an ion exchange group as a method of cheating out of the current-ratio resistance of a cation exchange membrane in the above-mentioned range by this invention, ****ing a degree of swelling to 65 - 110% of the weight by boiling or pressurizing and warming a cation exchange membrane in pure water, etc. can adopt preferably.

[0010] Although the cation exchange membrane of a perfluoro carbon polymer consists of a film of a monolayer preferably, the thickness has [making it be 30-300 micrometers and further 50-250 micrometers] a desirable thing. Since the handling nature in film intensity, electrode junction, etc. falls, a membrane resistance goes up and the output of a cell declines on the other hand when larger than a upper limit in being smaller than the above-mentioned lower limit, it is not desirable.

[0011] As a perfluoro carbon polymer containing the sulfonic group used for this invention, a copolymer with the fluoro vinyl compound expressed with a tetrafluoroethylene and $\text{CF}_2=\text{CF}-(\text{OCF}_2\text{CFX})_m-\text{Oq}-(\text{CF}_2)_n-\text{A}$ (inside of a formula $m=0-3$, $n=0-12$, $q=0$ or 1 , $X=\text{F}$ or CF_3 , $\text{A}=\text{sulfonic-acid type functional group}$) can adopt preferably. The compound shown in ** 1 is mentioned as a desirable example of the above-mentioned fluoro vinyl compound.

[0012]

[Formula 1]

CF₂=CFO(CF₂)₁₋₈ SO₂ FCF₂=CFOCF₂ CF(CF₃) O(CF₂)₁₋₈ SO₂ FCF₂=CF(CF₂)₀₋₈ SO₂ FCF₂=CF(OCF₂ CF(CF₃))₁₋₅ O(CF₂)₂ SO₂ F. [0013] In addition, a perfluoro olefin like hexafluoropropylene, a chlorotrifluoroethylene, and perfluoro alkoxy vinyl ether can also be used instead of the above-mentioned tetrafluoroethylene which is the monomer which constitutes a fluorocarbon polymer.

[0014] The cation exchange membrane which consists of the above-mentioned perfluoro carbon polymer film can also be reinforced with a perfluoro carbon polymer the shape of a fibril, the shape of textile fabrics, and nonwoven blanket-like.

[0015] The cation exchange membrane of this invention sticks a gas diffusion electrode on the front face according to the usual known technique, subsequently attaches a charge collector, and is assembled as a fuel cell. Although a gas diffusion electrode consists of a sheet of the porosity object which made the conductive carbon black powder which made the platinum-catalyst particle usually support hold by hydrophobic resin binding material, such as a polytetrafluoroethylene (PTFE), it may contain the particle by which this porosity object was covered with the sulfonic-acid type perfluoro carbon polymer or this polymer. A gas diffusion electrode and a sulfonic-acid type perfluoro carbon polymer are stuck by the hot press method etc. The conductive carbon board with which the slot where a charge collector serves as a path of fuel gas or oxidizer gas was formed is used.

[0016]

[Example] Based on the method indicated by JP,2-88645,A, the ion-exchange-capacity 1.1 milliequivalent / g dryness resin which consists of a copolymer of CF₂=CF₂ and CF₂=CFOCF₂ CFCF₃ O(CF₂)₂ SO₂ F were extruded at 220 degrees C, the film was produced, and the film with a thickness of 100 micrometers was obtained.

[0017] After hydrolyzing and rinsing the above-mentioned copolymer film in 30 % of the weight of dimethyl sulfoxide, and a 15 % of the weight [of caustic potash] mixed-water solution, it was immersed into the 1-N hydrochloric acid. Next, after rinsing the film and restraining the membranous neighborhood with an exclusive fixture, it dried for 1 hour and 60 degrees C of cation exchange membranes were manufactured. It was 8-ohmcm when the current-ratio resistance of this cation exchange membrane was measured.

[0018] The fuel cell property using this cation exchange membrane was evaluated. That is, PTFE was mixed in the carbon black powder which made the platinum-catalyst particle support, and the gas diffusion electrode of the shape of a sheet with a thickness of 250 micrometers was produced using the roll press. The membrane-electrode zygote was produced by inserting the above-mentioned cation exchange membrane and carrying out a laminating using a monotonous heat press machine between the gas diffusion electrodes of the two above-mentioned sheets. The amount of platinum catalysts of a membrane-electrode zygote is 2 1cm of film surface products. It was 1mg of hits.

[0019] Next, a membrane-electrode zygote is inserted from both sides in order of the charge collector made from titanium, the gas supply room made from PTFE, and a heater, and it is 2 9cm of effective film surface products. When the terminal voltage to the current density when having kept the temperature of the cell which finished setting up a fuel cell at 80 degrees C, supplying a positive electrode with oxygen and supplying hydrogen to a negative electrode with five atmospheric pressure, respectively was measured, it is current density 1 A/cm². It was cell voltage 0.65V.

[0020]

[Comparative Example(s)] Based on the method indicated by JP,2-88645,A, the ion-exchange-capacity 1.0 milliequivalent / g dryness resin which consists of a copolymer of CF₂=CF₂ and CF₂=CFOCF₂ CFCF₃ O(CF₂)₂ SO₂ F were extruded at 220 degrees C, the film was produced, and the film with a thickness of 100 micrometers was obtained. The same processing as an example was performed to this, and the cation exchange membrane was manufactured. The current-ratio resistance of this film was 12.6-ohmcm.

[0021] After finishing setting up a fuel cell by the same method as an example, when the terminal voltage to current density was measured under the same conditions, it is current density 1 A/cm². It was cell voltage 0.60V.

[0022] The cation exchange membrane of an example has the small energy loss when finishing setting up a fuel cell compared with the film of the example of comparison so that the above-mentioned result may show.

[0023]

[Effect of the Invention] By making into a solid-state polyelectrolyte the cation exchange membrane which has the low electric resistance which is not in a film conventionally, a highly efficient solid-state polyelectrolyte type fuel cell is obtained.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Based on the method indicated by JP,2-88645,A, the ion-exchange-capacity 1.1 milliequivalent / g dryness resin which consists of a copolymer of $\text{CF}_2=\text{CF}_2$ and $\text{CF}_2=\text{CFOCF}_2\text{CFCF}_3\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$ were extruded at 220 degrees C, the film was produced, and the film with a thickness of 100 micrometers was obtained.

[0017] After hydrolyzing and rinsing the above-mentioned copolymer film in 30 % of the weight of dimethyl sulfoxide, and a 15 % of the weight [of caustic potash] mixed-water solution, it was immersed into the 1-N hydrochloric acid. Next, after rinsing the film and restraining the membranous neighborhood with an exclusive fixture, it dried for 1 hour and 60 degrees C of cation exchange membranes were manufactured. It was 8-ohmcm when the current-ratio resistance of this cation exchange membrane was measured.

[0018] The fuel cell property using this cation exchange membrane was evaluated. That is, PTFE was mixed in the carbon black powder which made the platinum-catalyst particle support, and the gas diffusion electrode of the shape of a sheet with a thickness of 250 micrometers was produced using the roll press. The membrane-electrode zygote was produced by inserting the above-mentioned cation exchange membrane and carrying out a laminating using a monotonous heat press machine between the gas diffusion electrodes of the two above-mentioned sheets. The amount of platinum catalysts of a membrane-electrode zygote is 2 1cm of film surface products. It was 1mg of hits.

[0019] Next, a membrane-electrode zygote is inserted from both sides in order of the charge collector made from titanium, the gas supply room made from PTFE, and a heater, and it is 2 9cm of effective film surface products. When the terminal voltage to the current density when having kept the temperature of the cell which finished setting up a fuel cell at 80 degrees C, supplying a positive electrode with oxygen and supplying hydrogen to a negative electrode with five atmospheric pressure, respectively was measured, it is current density 1 A/cm². It was cell voltage 0.65V.

[0020]

[Comparative Example(s)] Based on the method indicated by JP,2-88645,A, the ion-exchange-capacity 1.0 milliequivalent / g dryness resin which consists of a copolymer of $\text{CF}_2=\text{CF}_2$ and $\text{CF}_2=\text{CFOCF}_2\text{CFCF}_3\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$ were extruded at 220 degrees C, the film was produced, and the film with a thickness of 100 micrometers was obtained. The same processing as an example was performed to this, and the cation exchange membrane was manufactured. The current-ratio resistance of this film was 12.6-ohmcm.

[0021] After finishing setting up a fuel cell by the same method as an example, when the terminal voltage to current density was measured under the same conditions, it is current density 1 A/cm². It was cell voltage 0.60V.

[0022] The cation exchange membrane of an example has the small energy loss when finishing setting up a fuel cell compared with the film of the example of comparison so that the above-mentioned result may show.

[Translation done.]